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A REARRANGEMENT IN THE REACTION OF *o*-CARBORANECARBOXYLIC ACID CHLORIDES WITH $NaFe(CO)_2C_5H_5$-π

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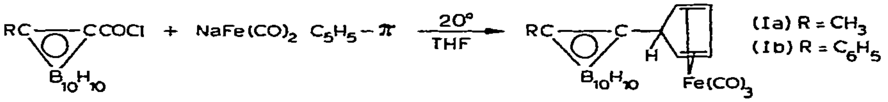
SUMMARY

A new rearrangement was discovered in the reaction of *o*-carboranecarboxylic acid chlorides with $NaFe(CO)_2C_5H_5$-π which led to [*exo*-(substituted-*o*-carboranyl)-cyclopentadiene]iron tricarbonyls. This rearrangement involves the formation of σ-acyl complex *o*-R–$CB_{10}H_{10}CCOFe(CO)_2C_5H_5$-$\pi$. Thermal transformations of these compounds to the binuclear iron complexes and their further conversion into the respective ferrocenes were investigated. It is interesting to note that 1,1′-(1,2-*o*-carboranylene)ferrocene has a rather large dihedral angle between the cyclopentadienyl ring planes. Reactions of *m*-carboranecarboxylic and *o*-carboranylacetic acid chlorides with $NaFe(CO)_2C_5H_5$-π resulted in the formation of σ-acyliron complexes which gave CO on heating and were transformed to the respective σ-iron derivatives.

Various carboxylic acid chlorides including those of perfluorinated carboxylic acids have been found to react with $NaFe(CO)_2C_5H_5$-π leading to the corresponding acyliron complexes[1,2]:

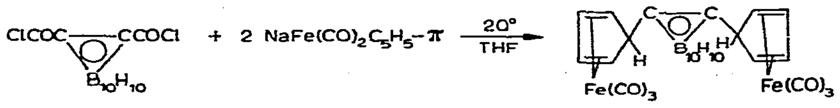
$$RCOCl + NaFe(CO)_2C_5H_5\text{-}\pi \rightarrow RCOFe(CO)_2C_5H_5\text{-}\pi$$

Thermal and photochemical decarbonylations of these complexes resulted in the formation of σ-alkyl- and aryliron complexes, σ-$RFe(CO)_2C_5H_5$-π thus providing a synthetic route to these compounds. In our previous communication[3] an attempt was made to employ this method for the preparation of σ-*o*-carboranyliron complexes. It has been shown that the substituted *o*-carboranecarboxylic acid chlorides abnormally gave substituted (*o*-carboranylcyclopentadiene)iron tricarbonyl complex(I):



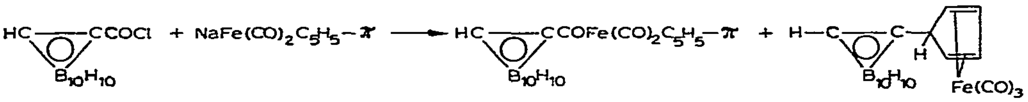
(I)

Analogously, *o*-carboranecarboxylic acid dichloride and $NaFe(CO)_2C_5H_5$-π led to the formation of bis(cyclopentadieneiron tricarbonyl) complex (II):



(II)

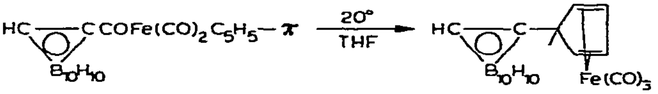
The reaction involves a rearrangement of *o*-carboranyl group with conversion of the π-cyclopentadienylic system to the π-cyclopentadienic one. Unlike substituted *o*-carboranecarboxylic acid chlorides the unsubstituted one was found to react with $NaFe(CO)_2C_5H_5$-π giving acyliron derivative (III) as the main product and a small amount of the rearrangement product (IV):



(III) (IV)

The reaction also gave *o*-carborane and (II) in small amounts.

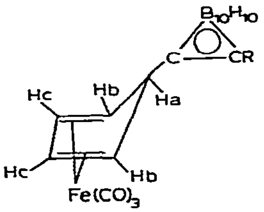
It was established that the acyl derivative (III) (stable in crystalline state) underwent slow rearrangement at 20° in THF or benzene to the product (IV) containing a cyclopentadienic system:



(III) (IV)

The rearrangement was found to be faster but less smooth on heating. In THF the rearrangement is somewhat faster than in benzene. Formation and the rearrangement of acyl complex (III) indicates that the reactions of substituted *o*-carboranecarboxylic acid chlorides with $NaFe(CO)_2C_5H_5$-π should also proceed through an intermediate formation of acyliron derivatives [analogous to complex (III)] which then undergo fast rearrangement to the π-cyclopentadienic structure. The facile nature of such a rearrangement with respect to that of (III) is probably due to the steric effect of a substituent in the *ortho*-position to the acyl group. Structure of (*o*-carboranylcyclopentadiene)iron tricarbonyl complexes was confirmed by their PMR and IR spectra. Proton chemical shifts of iron complexes prepared are listed in Table 1. Table 2 shows the IR data for the (*o*-carboranylcyclopentadiene)iron tricarbonyl complexes.

Structure of the cyclopentadienic complex (I) deduced from its PMR and IR spectra is shown below. Fig. 1 shows the PMR spectrum of compound (IV).

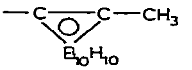
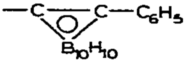
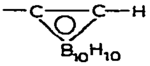
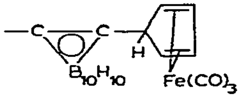


(I)

Besides the signals from substituent R the PMR spectra of (Ia), (Ib), (II) and (IV) exhibit three signals from the C_5H_5Fe group with relative intensities 2/2/1. "Triplet"

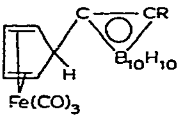
TABLE 1

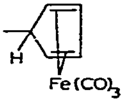
THE PROTON CHEMICAL SHIFTS OF CYCLOPENTADIENEIRON TRICARBONYL DERIVATIVES (δ, ppm from TMS)

Compound					
No.	R	Solvent	H_c	H_b	H_a
(Ia)		$CHCl_3$	5.60	3.18	3.18
		CH_2Cl_2		3.19	3.19
		C_6H_6	4.59	2.37	2.71
(Ib)		CCl_4	5.46	2.86	2.61
		$CHCl_3$	5.52	2.90	2.67
(IV)		C_6H_6	4.41	2.23	2.56
(II)		$CHCl_3$	5.58	3.14	3.11
		C_6H_6	4.62	2.92	2.47
	$-C_6F_5$[a]	$CDCl_3$	4.92	2.78	3.75
	$-H$[b]		5.62	2.85	2.69
					2.69

[a] Ref. 4. [b] Ref. 5.

TABLE 2

IR DATA FOR  IN CCl_4(cm^{-1})

Compound			
No.	R	ν(CO)	ν(CH)
(Ia)	$-CH_3$	1988, 2056	2875 m, 2930 w, 2950 w, 2960 m, 3070 w
(Ib)	$-C_6H_5$	1988, 2056	2878 w, 2950 s, 2960 m, 2998 w, 3070w
(IV)	$-H$	1990, 2057	2860 m, 2875 w, 2930 m (br), 2957 m, 3065 w, 3075 s
(II)		1988, 2057	2850 w, 2875 w, 2927 m, 2957 s, 3068 m

at δ 4.4–5.6 ppm and "quadruplet" at δ 2.2–3.2 ppm correspond to olefin protons of the H_c and H_b types which have essentially different shielding after formation of the π-complex. Multiplet at δ 2.4–3.2 ppm corresponding to the aliphatic H_a protons.

The ranges of shielding for protons H_b and H_a practically coincide, thus a required signal separation for each of (I), (II) and (VI) is attained by varying the solvent. Spin–spin coupling constants J_{cb}, $J_{cb'}$ and $J_{ab'}$ are close to those usually observed for metallocenes. Strictly speaking, the constants $1/2(J_{cb}+J_{cb'})$ and $1/3(J_{cb}+J_{cb'}+J_{ba})$

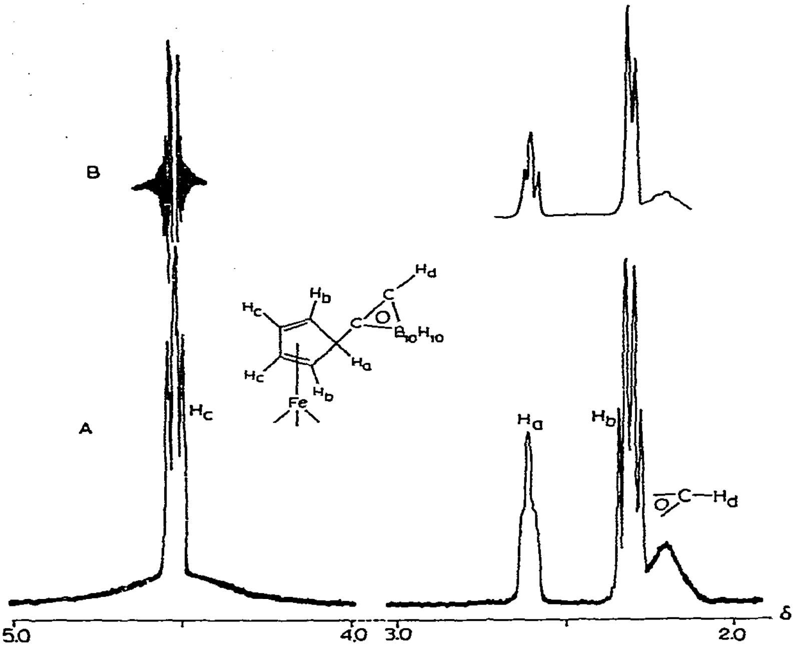


Fig. 1. A PMR spectrum of compound (IV) in benzene at room temperature (Varian HA-100D instrument). B. The same spectrum with double resonance of H_c signal.

are observed for triplet and quadruplet respectively. (Also there is a weak spin–spin H_c–H_a coupling influencing the shape of H_a proton signal and disappearing with irradiation of the signal H_c).

From the fact that both the observed constants are within 2–2.3 Hz it can be ascertained that the starting values J_{cb}, $J_{cb'}$ and J_{ba} which are usually obtained by calculation should be within 1–3 Hz. Thus under conditions of the markedly different shieldings of H_a and H_b protons the PMR spectra of C_5H_5Fe fragment for compounds (Ia), (Ib), (II) and (IV) might be discussed in the first order approximation and be assigned the spin system A_2M_2X ($J_{bc} \cong J_{b'c}$). These agree with a dienic structure of the five-membered cycle which is π-bonded to the iron atom.

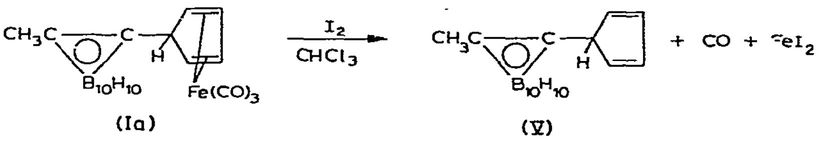
Analogous spectra were obtained for other π-cyclopentadienic compounds[4]. A comparison of the proton chemical shifts for (Ia), (Ib), (II) and (IV) with those of unsubstituted π-$C_5H_6Fe(CO)_3$[5] shows that introduction of the electron attracting carboranyl group decreases the shielding of all the three types of cyclopentadiene protons. The effect being most sensitive for H_a but does not influence the H_c and $H_{c'}$ protons. However such a comparison provides no information regarding which of the π-C_5H_6-$Fe(CO)_3$ protons (*exo* or *endo*) is replaced by the carboranyl group during formation of the complexes (I), (II) and (IV).

The IR spectra of (Ia), (Ib), (II) and (V) confirm a dienic structure. Comparison with the spectra of acyl derivatives of π-cyclopentadienyliron dicarbonyl shows a sharp change in the pattern. Firstly there is no intense CO acyl group absorption at 1600–1700 cm^{-1}, secondly, all the compounds exhibit a narrow band at 2056–2057 cm^{-1} and a broader one at 1988–1990 cm^{-1} in CCl_4 which is characteristic of $Fe(CO)_3$

group. These two bands refer respectively to the symmetric (A_1) and degenerate (E) CO ligand vibrations. For $Fe(CO)_3$ group the selection rules correspond to a local symmetry C_{3v}, which does not change despite the presence of dienic ligand in the molecule. $Fe(CO)_2$ group also shows two CO absorption bands shifted to the low frequency region as compared to the $Fe(CO)_3$ group. For compounds (I), (II) and (IV) the CO band positions are practically independent of substituent in the carborane nucleus probably due to its separation from the carboranyl ligands. Presence of two CO absorption bands in the spectrum of (II) is assigned to a weak vibration interaction of the CO groups at both iron atoms separated by carboranyl nucleus. The ν(C–H) of cyclopentadienyl ring normally absorbs at 3100 cm^{-1} and not below 3000 cm^{-1}. The spectra of (I), (II) and (IV) have more complex pattern and show the series of bands within 2800–3000 cm^{-1}. It is interesting to note that none of these compounds show absorption bands in the region 2750 cm^{-1}, which is commonly adopted[4–6] for the *exo*-CH group absorption of cyclopentadienic ligand. On the other hand all the compounds absorb at 2950 cm^{-1} which corresponds[4] to the *endo*-C–H bond vibrations. Thus the IR data allow to conclude that the compounds (Ia), (Ib), (II) and (IV) have the structure with *exo*-located carboranyl substituent.

Formation of single isomer with *exo*-substituent in cyclopentadiene ring in the course of rearrangement shows the strict stereospecificity of the reaction discovered.

Presence of the *o*-carboranyl–cyclopentadiene bond in complex (I) was confirmed also by chemical data. Reaction of iodine with (Ia) in $CHCl_3$ at 20° smoothly gives 1-methyl-2-cyclopentadienyl-*o*-carborane (V):



According to the PMR data the reaction leads to a mixture of isomers (V) with different locations of double bonds with respect to the methyl-*o*-carboranyl group.

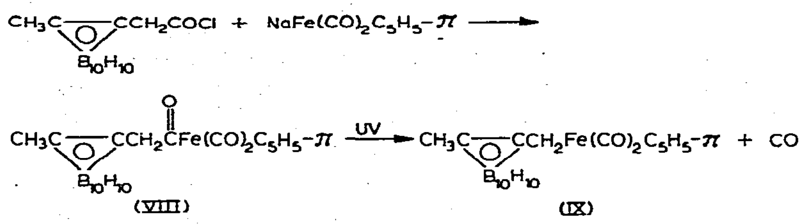
Unlike *o*-carboranecarboxylic acid chlorides, *m*-carborane carboxylic acid chlorides react in a normal way with $NaFe(CO)_2C_5H_5$-π giving only the σ-acyliron derivative (VI). The latter readily loses CO on heating in xylene giving σ-*m*-carboranyliron complexes (VII):

$$m\text{-}HCB_{10}H_{10}CCOCl + NaFe(CO)_2C_5H_5\text{-}\pi \rightarrow \underset{\text{(VI)}}{m\text{-}HCB_{10}H_{10}CCOFe(CO)_2C_5H_5\text{-}\pi}$$

$$\xrightarrow{t^{o}} \underset{\text{(VII)}}{m\text{-}HCB_{10}H_{10}CFe(CO)_2C_5H_5\text{-}\pi} + CO$$

Unlike the *o*-carboranyl derivatives, (VI) underwent no rearrangement on heating.

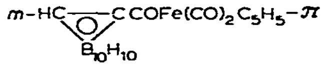
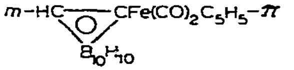
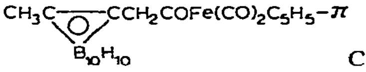
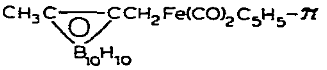
In the same manner (2-methyl-*o*-carboranyl)acetyl chloride normally reacts with $NaFe(CO)_2C_5H_5$-π leading to the formation of acyliron complex (VIII). Its thermal decarbonylation afforded only traces of (2-methyl-*o*-carboranyl)methyliron complex (IX) along with other decomposition products. UV irradiation of (VIII) in thiopene free benzene gave (IX) (70%).


(VIII) (IX)

It should be noted that unlike compound (VI) the decarbonylation in this case is much harder to proceed.

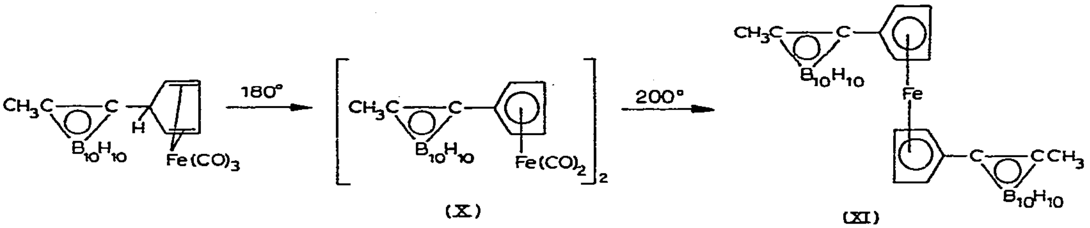
TABLE 3

PMR AND IR DATA FOR σ-ACYL- AND σ-CARBORANE IRON COMPLEXES

No.	Compound	Solvent	δ(ppm from TMS)			ν(cm^{-1})	
			C_5H_5	CH_3	CH_2	Co ligand (CCl_4)	Acyl group (KBr)
(III)		CCl_4	4.96			1992, 2041	1625
(VI)		C_6H_6	4.02			1984, 2036	1625
(VII)		C_6H_6	3.81			1992, 2037	
(VIII)		$CHCl_3$ C_6H_6	4.93 4.07	1.99 1.42	3.61 3.29	1970, 2025	1660
(IX)		CCl_4 $CHCl_3$	4.92 4.92	2.05 2.06	2.05 2.06	1971, 2023	

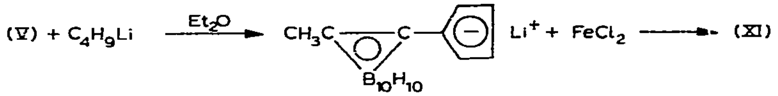
Structures of compounds (III), (VI), (VII), (VIII) and (IX) were confirmed by their PMR and IR spectra which are presented in Table 3. All the PMR spectra exhibit a narrow signal at δ 3.81–4.96 ppm (with a relative intensity equal to 5) assigned to the cyclopentadienyl ligand π-bonded to the iron atom. The single signals of the groups H, CH_2 and CH_3 which are directly adjacent to the carbon atoms of carborane were found to be somewhat broader due to a weak interaction with its magnetically active nuclei. In the IR spectra of (III), (VI) and (VIII) the CO acyl group absorption appears at 1625–1660 cm^{-1}, but it does not show for (VII) and (IX). All the other compounds exhibit two bands of the $Fe(CO)_2$ group carbonyl ligands in the regions of 1970–1992 and 2025–2041 cm^{-1}.

Earlier only two cyclopentadienyltricarbonyl complexes such as unsubstituted $C_5H_6Fe(CO)_3$[5] and *exo*-(1-C_6F_5)$C_5H_5Fe(CO)_3$[4] (obtained in a rather low yield) were known. $C_5H_6Fe(CO)_3$ is an unstable compound slowly darkening when stored in air. Complexes (I), (II) and (IV) are more stable and do not change upon long storage in air and even after 10 h in refluxing benzene under argon. On heating to 180° in decaline, (Ia) loses CO giving the binuclear complex (X). The latter on further heating to 200° transforms to 1,1'-bis(2-methyl-*o*-carboranyl)ferrocene (XI).

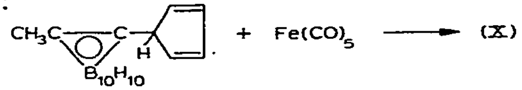


(X) (XI)

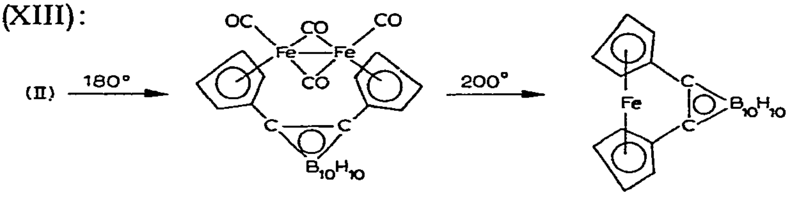
Compound (XI) was synthesized also from (V):



(X) was obtained from (2-methyl-*o*-carboranyl)cyclopentadiene (V) and $Fe(CO)_5$:



Prolonged heating of (II) at 180° gives intermolecular binuclear complex (XII) which then affords 1,1'-(1,2-*o*-carboranylene)ferrocene on further heating to 200° (XIII):



(XII) (XIII)

The compound (XIII) is well soluble in benzene, diethyl ether but somewhat poorer in heptane and ethanol. It is stable in air. The UV irradiation of complex (II) gives binuclear complex other than (XII). Its poor solubility in common solvents prevented its structural investigation. Structures of (X), (XI), (XII) and (XIII) were confirmed by their PMR and IR spectra. The PMR and IR data for these compounds are presented in Table 4.

TABLE 4 PMR AND IR DATA FOR SOME SUBSTITUTED FERROCENES AND BINUCLEAR IRON COMPLEXES

Compound	Solvent	δ (ppm from TMS)		ν(cm⁻¹)(CCl₄)	
		C_5H_4	CH_3	Bridged CO	Terminal CO
(XI)	$CHCl_3$	4.47	1.49		
(XIII)	CCl_4	3.97, 5.61			
(XII)	C_6H_6	4.58, 4.26		1795 m	1978 m, 2015 s
(X)				1783 m	1988 s, 2056 s

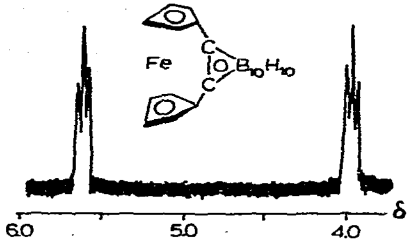


Fig. 2. PMR spectrum of cyclopentadienyl protons in 1,1'-(1,2-*o*-carboranylene)ferrocene (XIII) (in CCl_4).

The PMR spectra of (XI), (XII) and (XIII) show signals in the region of cyclopentadienyl ligand π-bonded to the iron atom but have some specific features. Interesting specificity was observed in the spectrum of (XI). Strong electron-attracting character of its *o*-carborane nucleus causes substantial deshielding of the cyclopentadienyl protons. But actually such an effect is practically the same for the protons close or further with respect to a substituent as we did not observe any separation of their signals. This specificity answers why the complex (XIII) has principally different spectrum (Fig. 2): two far separated triplets of the spin system A_2X_2 ($J_{ab} \cong J_{ab'}$) with $J = 1/2(J_{ab} + J_{ab'}) = 2$ Hz, and an internal H_a and H_b proton chemical shift of about 1.6 ppm. Apparently, owing to structural specificity (XIII) has noticeable dihedral angle between the cyclopentadienyl rings. As a result, each type of proton has substantially different separations from the iron equatorial molecular plane which leads to such large Δδ. Similar spectral effect due to the constrained incline of ferrocene rings has been reported in a number of papers[7,8]. Thus 1,1,2,2-tetramethyl-2-ferrocenophane[7] shows Δδ for the H_a and H_b proton chemical shifts equal to 0.54 ppm with a dihedral angle of 23° between the ring planes.

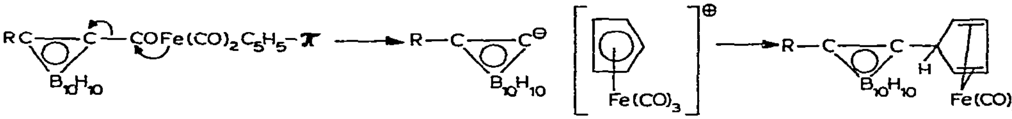
For compound (XIII) there is an essential difference in the chemical shifts for the H_a and H_b protons which together with molecular geometry of (XIII) indicates that cyclopentadienyl rings may be more inclined in this compound than in 1,1,2,2-tetramethyl-2-ferrocenophane. The PMR spectrum of (XII) also had two triplets with an internal chemical shift of about 0.3 ppm which can not be explained without further detailed investigations.

Within the region of stretching vibrations CO the IR spectrum of (X) in CCl_4 resembles that of $[Fe(CO)_2Cp]_2$ which has *cis*-structure in solution[9,10]. In solution it shows two bands at 1961 and 2005 cm^{-1} due to terminal CO groups and the band due to asymmetric vibrations of bridged CO groups at 1794 cm^{-1} (in octane). Analogously (X) absorbs in CCl_4 at 1988, 2056 and 1783 cm^{-1}, respectively. Shift of absorption of terminal CO groups towards higher frequencies results from the strong attracting effect of a carborane substituent in cyclopentadienyl ring. The latter absorbs at 3130 (C–H stretching vibrations), 1415 (ring bending modes) and within 800–900 cm^{-1} (out-of-plane C–H bending modes). The IR spectrum of (XII) in the CO stretching region is also rather close to that of *cis*-$[Fe(CO)_2Cp]_2$. It shows one asymmetric vibration band at 1795 cm^{-1} due to the bridged CO groups and two bands of terminal CO groups at 1978 and 2015 cm^{-1} (in CCl_4). With respect to $[Fe(CO)_2Cp]_2$ the spectrum of (XII) has other relative intensities for absorption of the terminal CO groups. If in $[Fe(CO)_2Cp]_2$ they are almost equal then in (XII) the high frequency band (symmetric CO stretching vibrations) is of much higher intensity than the low frequency band (asymmetric CO stretching vibrations). Probably in (XII) this is due to a decrease in the terminal CO angle after insertion of bulky carborane substituent between two cyclopentadienyl rings. If in $[Fe(CO)_2Cp]_2$ the ratio of the band intensities shows that for two terminal groups the angle is almost obtuse then in (XII) it is essentially less than 90°.

IR spectrum of (XI) exhibits the bands at 3110–3125 cm^{-1}, 820–840 cm^{-1} and 460–480 cm^{-1} characteristic of ferrocene system. Absence of the absorption at 1000 cm^{-1} confirms the presence of substituents in both the rings. The carborane nucleus shows very strong absorption at 2600 cm^{-1}.

In the IR spectrum of (XIII) there are the bands characteristic of ferrocene: ν(C–H) at 3100 cm^{-1} (three bands) and the out of plane C–H bending vibrations at 810 and 820 cm^{-1}. Both cyclopentadienyl rings in (XIII) are substituted which is evident from the absence of absorption at 1000 cm^{-1} and at 1100 cm^{-1}. However the spectrum of (XIII) differs somewhat from those of Cp_2Fe and (XI). Significant change is observed in the Fe–Cp stretching absorptions. For Cp_2Fe and (XI) these bands appear at 480 cm^{-1} while in (XIII) they are shifted to a higher frequency region of 515–525 cm^{-1}. The spectrum pattern in the region of the CH stretching and bending vibrations is different from those of ferrocene and (XI). Both these factors indicate a certain alteration in the Fe–Cp bond character due to a change in the dihedral angle between the cyclopentadienyl rings.

At present we have no feasable explanation for a mechanism of the rearrangement discovered. But it can be assumed that in an intermediate acyl derivative factors such as strong electron-attracting effect, steric strain and stability of *o*-carborane anion cause an electron transfer from iron to carbonyl nucleus producing *o*-carboranyl anion and cyclopentadienyliron tricarbonyl cation in the transition state. The cation then transforms to the cyclopentadiene system.



Formation of [*exo*-(perfluorophenyl)cyclopentadiene]iron tricarbonyl[4] from (perfluorophenyl)lithium and $C_5H_5Fe(CO)_3^+$ PF_6^- may serve as an evidence for this scheme.

EXPERIMENTAL

The PMR spectra were recorded on Perkin–Elmer R-12 (60 MHz) and Varian HA-100 D (100 MHz) spectrometers. Chemical shifts are given within an accuracy of ± 0.01 ppm in δ scale. IR spectra were recorded as KBr pellets or in CCl_4 solution on UR-20 "Zeiss" instrument. It was calibrated using the polystyrene spectrum and vibrational/rotational spectrum of gaseous DCl (near 2000 cm^{-1}).

Reactions were carried out under a stream of dry argon. THF was distilled over $LiAlH_4$.

Reactions of substituted o-carboranecarboxylic acid chlorides with $NaFe(CO)_2C_5H_5$-π

0.02 mole of substituted *o*-carboranecarboxylic acid chloride in 50 ml THF was added with stirring to 0.02 mole $NaFe(CO)_2C_5H_5$-π in 75 ml THF at −60°. After 1 h the mixture was heated to 20° and allowed to stay overnight. THF was evaporated *in vacuo*, the residue chromatographed on alumina column (the II-nd activity grade) and eluted with petroleum ether (b.p. 40–70°). The products were crystallized from hexane.

[exo-(2-Methyl-o-carboranyl)cyclopentadiene]iron tricarbonyl (Ia). M.p. 177–178° (decompn.), yield 65%. (Found: C, 36.43; H, 5.21; B, 29.96; Fe, 15.39. $C_{11}H_{18}B_{10}FeO_3$ calcd.: C, 36.36; H, 5.01; B, 29.86; Fe, 15.42%.)

[exo-(2-Phenyl-o-carboranyl)cyclopentadiene]iron tricarbonyl (Ib). M.p. 165–166° (decompn.), yield 40%. (Found: C, 45.34; H, 4.92; B, 25.54; Fe, 12.68. $C_{16}H_{20}B_{10}FeO_3$ calcd.: C, 45,28; H, 4.75; B, 25.50; Fe, 13.16%.)

(Carboranylenebisyclopentadiene)bis(iron tricarbonyl)(II). M.p. 186–187° (decompn.), yield 70%. (Found: C, 39.23; H, 3.56; B, 19.68. $C_{18}H_{20}B_{10}Fe_2O_6$ calcd.: C, 39.15; H, 3.65; B, 19.59%.)

Reaction of o-carborane carboxylic acid chloride with $NaFe(CO)_2C_5H_5$-π

The reaction was carried out analogously to (I) and (II). Chromatography on alumina column gave the mixture of products (solvent petroleum ether) and (III) (solvent benzene). Yield of (III) 30%. M.p. 106–107° (heptane). (Found: C, 34.01; H, 4.60; B, 31.80; Fe, 16.48. $C_{10}H_{16}B_{10}FeO_3$ calcd.: C, 34.49; H, 4.64; B, 31.04; Fe, 16.03%.)

From the mixture of products *o*-carborane was sublimed (7% based on starting acid chloride). (II) and (IV) (3%) were found in the residue as shown by means of PMR spectra.

Rearrangement of (o-carboranecarbonyl)-π-cyclopentadienyliron dicarbonyl (III) to (exo-o-carboranylcyclopentadiene)iron tricarbonyl (IV)

A solution of 0.2 g (III) in 30 ml THF was allowed to stay at 20° for 10 days under an atmosphere of argon. THF was removed *in vacuo* and the residue chromatographed on alumina column, solvent: petroleum ether (b.p. 40–70°). 0.1 g (IV) was isolated M.p. 170–171.5° (heptane). (Found: C, 33.81; H, 4.83; B, 31.40; Fe, 16.37. $C_{10}H_{16}B_{10}FeO_3$ calcd.: C, 34.49; H, 4.64; B, 31.04; Fe, 16.03%.)

From the mother liquor very small amount of *o*-carborane was isolated by recrystallization and sublimation.

Synthesis of σ-(m-carboranecarbonyl)-π-cyclopentadienyliron dicarbonyl (VI) and [(2-methyl-o-carboranyl)acetyl]cyclopentadienyliron dicarbonyl (VIII)

Syntheses were conducted analogously to those of (I)–(IV). (VI) was purified by recrystallization from hexane/acetone (1/1) M.p. 158–159°. Yield 50% (Found: C, 34.81; H, 4.68; B, 31.06; Fe, 15.95. $C_{10}H_{16}B_{10}FeO_3$ calcd.: C, 34.49; H, 4.62; B, 31.04; Fe, 16.03%.)

(VIII) was crystallized from heptane/ether (1/1). M.p. 116–117°. Yield 35%. (Found: C, 38.83; H, 4.99; B, 28.66; Fe, 14.13. $C_{12}H_{20}B_{10}FeO_3$ calcd.: C, 38.3; H, 5.36, B, 28.73; Fe, 14.84%.)

Decarbonylation of (VI)

0.5 g (VI) in 30 ml of *p*-xylene was refluced for 4 h. 55 ml of CO was evolved. Xylene was evaporated *in vacuo*. The residue was chromatographed on alumina column, (benzene/hexane 1/1). 0.35 g of σ-*m*-carboranylcyclopentadienyliron dicarbonyl (VII) was isolated. M.p. 88–89°. (Found: C, 33.39; H, 5.07; B, 33.82; Fe, 17.47. $C_9H_{16}B_{10}FeO_2$ calcd.: C, 33.75; H, 5.05; B, 33.76; Fe, 17.44%.)

Decarbonylation of (VIII)

0.4 g (VIII) in 30 ml benzene was UV irradiated for 4 h. 30 ml of CO was evolved. Benezene was evaporated *in vacuo* and the residue recrystallized from petroleum ether/ether (1/1). 0.25 g (IX) was isolated. B.p. 140–143°. (Found: C, 37.50; H, 5.81; B, 30.94; Fe, 16.73. $C_{11}H_{20}B_{10}FeO_2$ calcd.: C, 37.93; H, 5.8; B, 31.04; Fe, 16.03%.)

Reaction of [exo-(2-methyl-o-carboranyl)cyclopentadiene]iron tricarbonyl (Ia) with I_2

A solution of 2.5 g I_2 in 100 ml $CHCl_3$ was added at 20° with stirring to 2 g (Ia) in 100 ml $CHCl_3$. After 5 h, $CHCl_3$ was evaporated, the residue extracted with petroleum ether, washed with 10% sodium bisulfite solution and dried over $CaCl_2$. 1 g of (2-methyl-*o*-carboranyl)cyclopentadiene (V) was obtained. It was recrystallized from pentane. M.p. 100–101°. (Found: C, 43.75; H, 8.32; B, 48.3. $C_8H_{18}B_{10}$ calcd.: C, 43.19; H, 8.17; B, 48.63%.)

Thermal decomposition of (Ia)

1 g (Ia) in 30 ml of decaline was heated at 180° for 15 h. Precipitated black crystals of bis{[(2-methyl-*o*-carboranyl)cyclopentadienyl]iron dicarbonyl}(X) were filtered off and washed with diethyl ether. Yield 50%. No elemental analysis was conducted for (X) because its insolubility in common solvents prevented its purification. Decaline was evaporated *in vacuo* and the residue recrystallized from pentane/ether (1/1). 0.2 g of 1,1'-bis(2-methyl-*o*-carboranyl)ferrocene (XI) was obtained. M.p. 249–250°. (Found: C, 38.53; H, 7.24; B, 43.57; Fe, 11.01. $C_{16}H_{34}B_{20}Fe$ calcd.: C, 38.54; H, 6.88; B, 43.10; Fe, 11.2%.)

Reaction of (2-methyl-o-carboranyl)cyclopentadiene (V) with $Fe(CO)_5$

0.25 g (V) in dibutyl ether was heated with 0.4 g $Fe(CO)_5$ for 8 h, then 0.2 g of $Fe(CO)_5$ was added and the mixture was heated for 10 h. Precipitated solid was filtered off and washed several times with diethyl ether. (X) was obtained in 50% yield.

Synthesis of 1,1'-*bis(2-methyl-o-carboranyl) ferrocene (XI)*

Method A. 0.2 g of (X) was refluxed in decaline for 12 h. Decaline was evaporated *in vacuo*, and the residue recrystallized from pentane/ether mixture (1/1). Yield of (XI) was 70%.

Method B. 1 ml of 1 *N* BuLi in benzene was added with stirring to 0.2 g of (V) in 10 ml of absolute ether. After 1 h the solution of lithium derivative was poured to a suspension of 0.2 g of $FeCl_2$ in 50 ml of ether. After 12 h the reaction mixture was poured on ice containing hydrochloric acid, the ethereal layer was washed with water and dried over $CaCl_2$; 0.15 g of (XI) was isolated.

Thermal decomposition of (carboranylenedicyclopentadiene)bis(iron tricarbonyl) (II)

1 g of (II) was heated in decaline at 180° for 20 h. Decaline was evaporated *in vacuo* and petroleum ether was added to the residue. Black insoluble crystals were filtered off and washed with petroleum ether. 0.4 g of binuclear complex (XII) was isolated. M.p. 238–239° (decompn.). [ether/heptane(1/1). (Found: C, 39.21; H, 3.96; B, 21.83. $C_{18}H_{18}Fe_2O_4$ calcd.: C, 38.88; H, 3.67; B, 21.88%.)

Synthesis of 1,1′-(1,2-*o-carboranylene*)*ferrocene* (*XIII*)

1 g of (XII) was refluxed in decaline for 30 h. Decaline was evaporated *in vacuo*. The residue on extraction with heptane gave (XIII) (35 %). M.p. 229–230 % (pentane). (Found: C, 44.10; H, 5.55; B, 32.65; Fe, 16.94. $C_{12}H_{18}B_{10}Fe$ calcd.: C, 44.19; H, 5.57; B, 33.13; Fe, 17.12 %.)

REFERENCES

1 R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, 2 (1964) 15.
2 R. B. King, *Advan. Organometal. Chem.*, 2 (1964) 157.
3 L. I. Zakharkin, A. I. Kovredov, L. V. Orlova, L. A. Fedorov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1969) 2343.
4 P. M. Treichnel and R. L. Schubkin, *Inorg. Chem.*, 6 (1967) 1323.
5 R. K. Kochnar and R. Pettit, *J. Organometal. Chem.*, 6 (1966) 272.
6 J. U. Khand, P. L. Pauson and W. E. Watts, *J. Chem. Soc. (C)*, (1969) 2024.
7 T. H. Barr and W. E. Watts, *Tetrahedron*, 24 (1968) 6111.
8 H. L. Lentzner and W. E. Watts, *Chem. Commun.*, (1970) 26.
9 F. A. Gotton and G. Yagupsky, *Inorg. Chem.*, 6 (1967) 15.
10 R. D. Fischer and A. Vogler, *J. Organometal. Chem.*, 7 (1967) 135.